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(54) **Polyethylene stabilizer compositions comprising compounds with piperidine groups and metal compounds**

Polyäthylen-Stabilisatorzusammensetzungen aus Verbindungen mit Piperidin gruppen und Metalverbindungen

Compositions stabilisantes de polyéthylène à base de composés avec des groupements de pipéridine et composés de métal

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(56) References cited:
GB-A- 2 132 621

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- PATENT ABSTRACTS OF JAPAN, vol. 11, no. 124 (C-416)[2571], 17th April 1987; & JP-A-61 261 332 (SUMITOMO NAUGATUCK CO., LTD) 19-11-1986

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Designated Contracting States:
IT

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Description

The present invention relates to a novel method for stabilizing polyethylene against photooxidative degradation by using mixtures of 2,2,6,6-tetramethylpiperidine derivatives and particular metal compounds.

5 Polyethylene is here to be understood as meaning linear or branched polymers of ethylene of low, medium and high density, their mixtures in any proportions and also ethylene copolymers with aliphatic C₃-C₁₂- α -olefines containing up to 20% of di- α -olefines.

10 Of particular interest are branched low-density polyethylene, generally known as LDPE, and linear low-density polyethylene, generally designated as LLDPE, and their mixtures in any proportion.

15 It is known that polyethylene undergoes a progressive decrease in mechanical strength up to embrittlement when it is exposed to sunlight, as a result of photooxidative degradation caused by ultraviolet radiation.

To overcome this drawback it is necessary to add to the polymer suitable light stabilizers, for example certain derivatives of benzophenone and benzotriazole, nickel complexes, esters of substituted benzoic acids or sterically hindered amines.

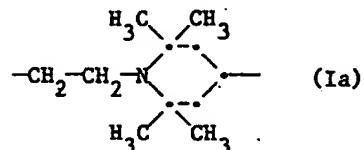
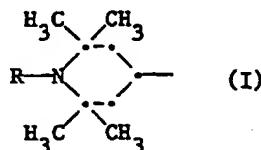
15 Certain 2,2,6,6-tetramethylpiperidine derivatives of relatively high molecular weight have recently shown remarkable efficacy; nevertheless, the results obtained with these compounds have not been completely satisfactory, so that a further improvement was desirable.

It has now been found surprisingly that, when particular mixtures of one or more 2,2,6,6-tetramethylpiperidine derivatives with one or more metal compounds are used, light stability values are obtained which are significantly higher than those given by the use of piperidine compounds alone.

20 In particular, the present invention relates to a novel method for stabilizing polyethylene, which comprises the use of synergistic mixtures composed of

(A) one or more compounds with groups of the formula (I) or (Ia)

25



35 in which R is hydrogen, C₁-C₄-alkyl, allyl, benzyl, acetyl, acryloyl, 2-hydroxyethyl or 2-hydroxypropyl, said piperidine group of formula (I) not being bound in the 4-position to an oxygen atom, preferably hydrogen or methyl, and (B) one or more metal compounds selected from oxides and hydroxides of Al, Mg and Zn, preferably Mg and Zn.

If appropriate, the following can be added to the mixtures of (A)+(B):

40 (C) one or more salts of Al, Ba, Ca, Mg, Sr and Zn with C₁-C₂₂-carboxylic acids, preferably the salts of Al, Ca, Mg or Zn with C₁₂-C₁₈-carboxylic acids. The use of certain 2,2,6,6-tetramethylpiperidine derivatives mixed with oxides or hydroxides of Mg or Zn as stabilizers for polymers was already known, but was restricted to the stabilization of polyurethanes.

45 In particular, Japanese Patent 82-34,155, published on 24.2.1982, claims the stabilization of polyurethanes with mixtures comprising esters of 2,2,6,6-tetramethyl-4-piperidinol, oxides or hydroxides of Mg or Zn and organic phosphites. The said mixtures do not give satisfactory results when used for stabilizing polyethylene.

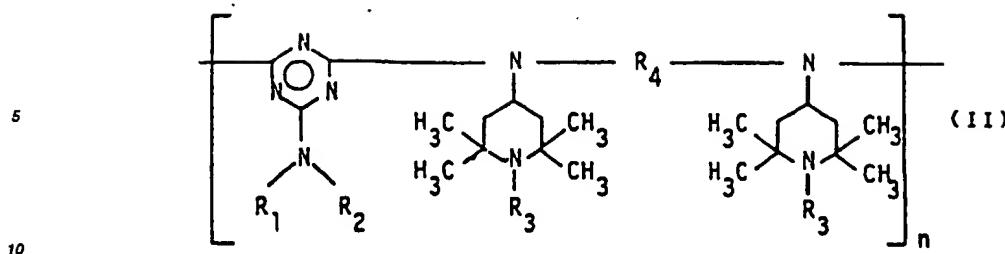
D.S. Carr and B. Baum (Modem Plastics, 7/1981, p. 64-68; C.A. 95, 81924) describe a light stabilizing system based on the combination of zinc dimethyl- or diethyl-dithiocarbamate and zinc oxide for use in plastics.

50 On the other hand, British Patent 2,132,621 describes the use of mixtures of zinc oxide and esters of 2,2,6,6-tetramethyl-4-piperidinol as photodegrading agents for polyolefines, in particular polyethylene and polypropylene.

The synergistic light stabilizing effect, obtained with the mixtures of the present invention, on polyethylene is therefore surprising.

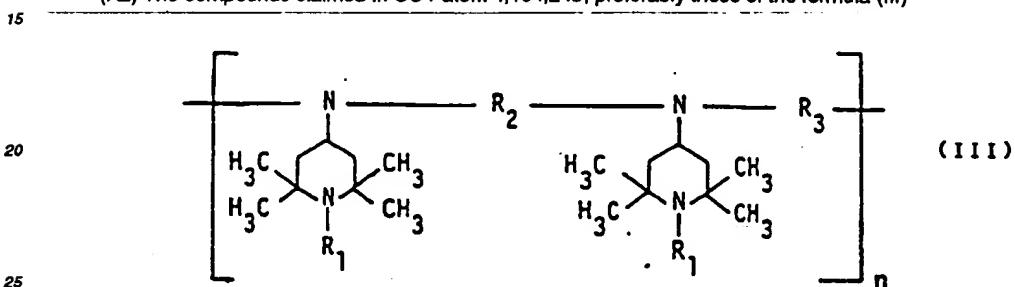
55 Compounds (A) which contain the group of the formula (I) or (Ia) and can be used according to the present invention are:

(A1) The compounds claimed in US Patent 4,086,204, preferably those of the formula (II)



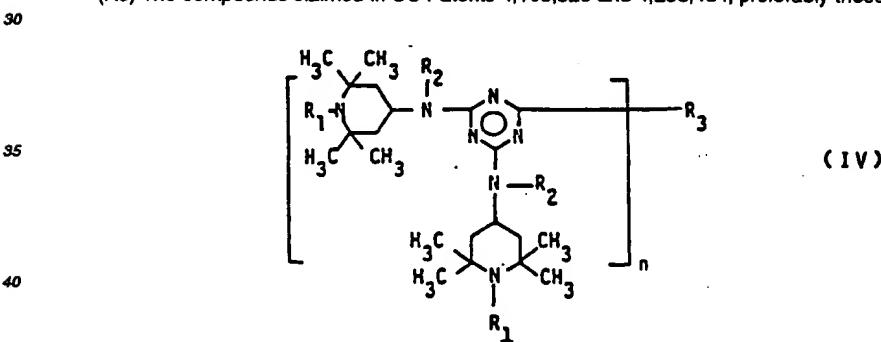
in which R_1 is C_1 - C_8 -alkyl, cyclohexyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, R_2 is hydrogen or C_1 - C_8 -alkyl, R_3 is hydrogen or methyl, R_4 is C_2 - C_6 -alkylene and n is a number from 2 to 20;

(A2) The compounds claimed in US Patent 4,104,248, preferably those of the formula (III)



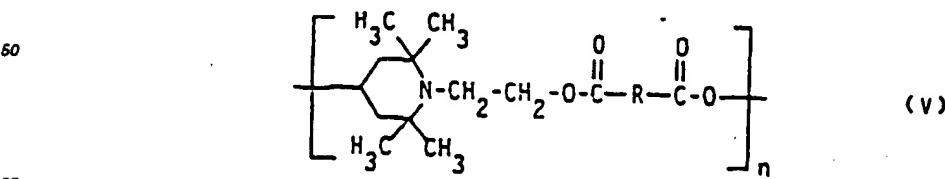
in which R_1 is hydrogen or methyl, R_2 is C_2 - C_6 -alkylene, R_3 is C_2 - C_6 -alkylene, 2-hydroxytrimethylene or xylylene and n is a number from 2 to 20;

(A3) The compounds claimed in US Patents 4,108,829 and 4,263,434, preferably those of the formula (IV)



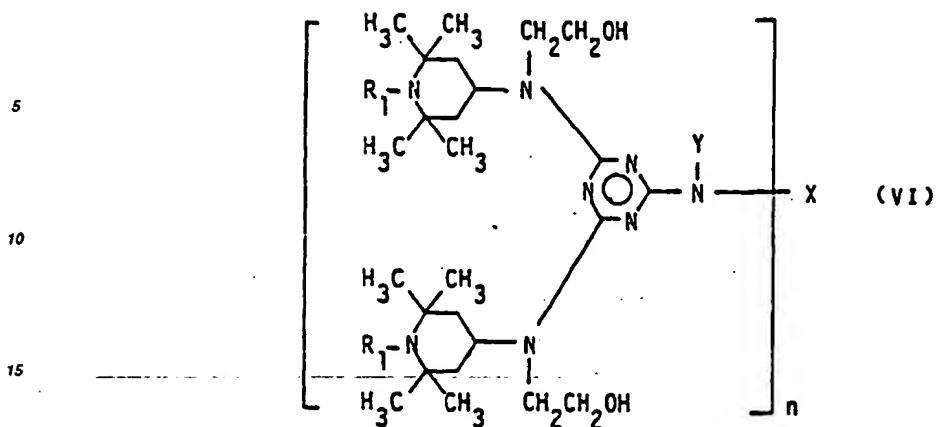
in which R_1 is hydrogen or methyl, R_2 is hydrogen, C_1 - C_8 -alkyl, cyclohexyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, n is 2, 3 or 4 and R_3 is the radical of an n-valent polyamine;

(A4) The compounds claimed in US Patent 4,233,412, preferably those of the formula (V)

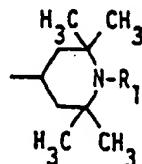


in which R is C_2 - C_8 -alkylene and n is a number from 2 to 30;

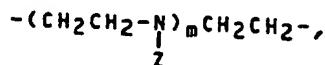
(A5) The compounds claimed in European Patent 22,080, preferably those of the formula (VI)



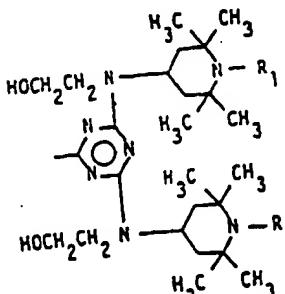
in which R_1 is hydrogen or methyl, n is 1 or 2, with $n = 1$ X is C_1-C_{12} -alkyl, benzyl or $-CH_2CH_2OH$ and Y is hydrogen or a group



and with $n = 2$ X is C_2-C_6 -alkylene, xylene or a group

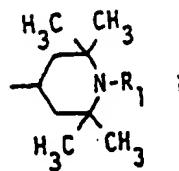


where m is 1 or 2 and Z is a group of the formula



and Y is hydrogen or a group

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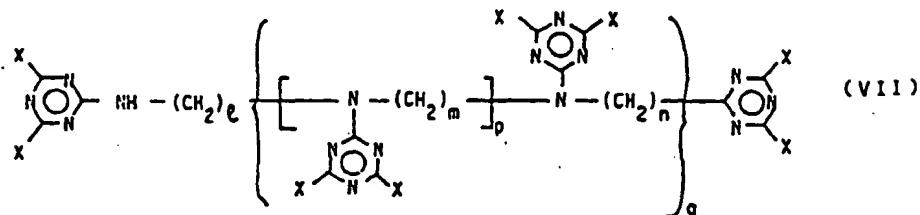


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(A6) The compounds claimed in European Patent 29,522, preferably those of the formula (VII)

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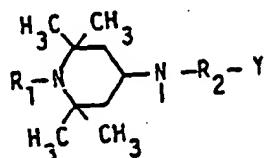
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in which l, m, n are 2 or 3, p and q are zero or 1 and X is a group

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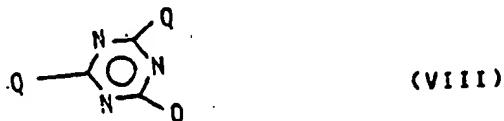
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where R1 is hydrogen or methyl, R2 is C2-C3-alkylene and Y is OH, C1-C8-alkoxy, dimethylamino or diethylamino;

(A7) The compounds claimed in US Patent 4,288,593, preferably those of the formula (VIII)

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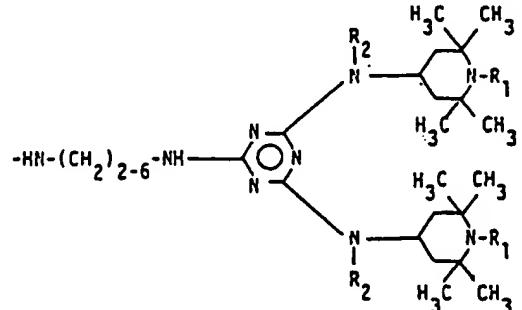


in which Q is a group of the formula

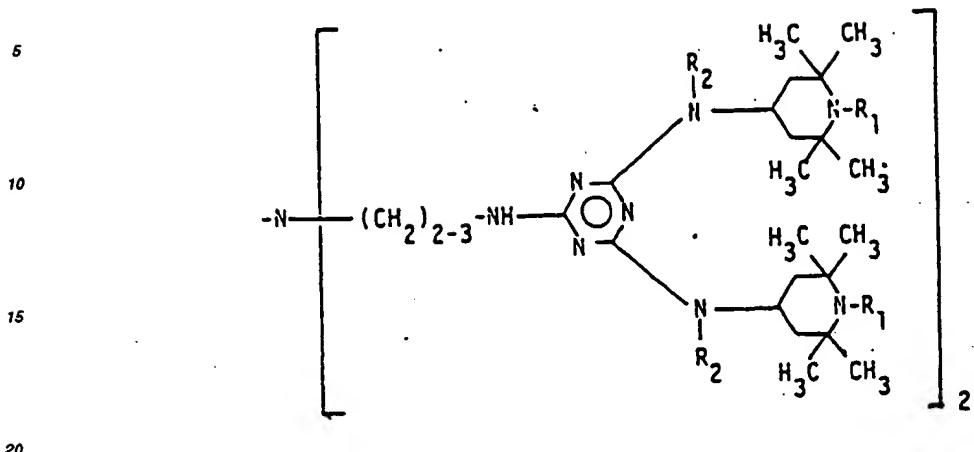
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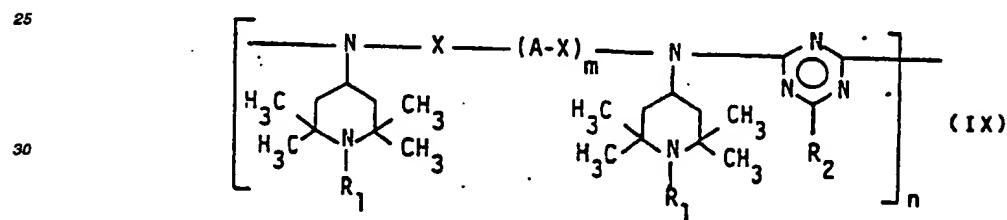
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or a group of the formula



where R_1 is hydrogen or methyl and R_2 is C_1 - C_8 -alkyl;
 (A8) The compounds claimed in US Patent 4,315,859, preferably those of the formula (IX)



in which R_1 is hydrogen or methyl, X is C_2 - C_6 -alkylene, A is $-O-$, $-NH-$ or



m is 1 or 2, R_2 is morpholino, hexamethyleneimino, $-OR_3$ or

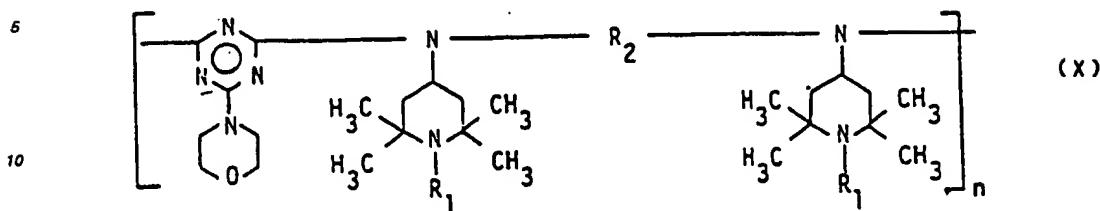


60 where R_3 is C_1 - C_8 -alkyl allyl, cyclohexyl, phenyl or benzyl and R_4 and R_5 which can be identical or different are C_1 - C_8 -alkyl which may be interrupted by an oxygen atom, allyl, cyclohexyl, 2-hydroxyethyl, benzyl or a group



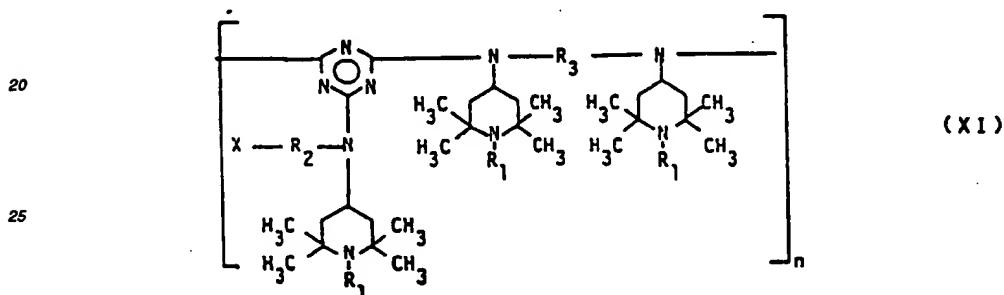
and R₆ can also be hydrogen;

(A9) The compounds claimed in US Patent 4,331,586, preferably those of the formula (X)



in which R₁ is hydrogen or methyl, R₂ is C₂-C₆-alkylene and n is a number from 2 to 20;

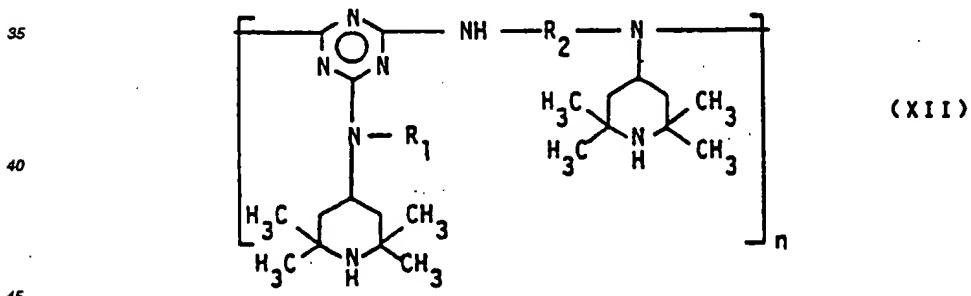
(A10) The compounds claimed in European Patent 24,338, preferably those of the formula (XI)



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in which R₁ is hydrogen or methyl, R₂ is C₂-C₃-alkylene, X is C₁-C₈-alkoxy, dimethylamino or diethylamino, R₃ is C₂-C₆-alkylene and n is a number from 2 to 20;

(A11) The compounds claimed in European Patent 42,554, preferably those of the formula (XII)

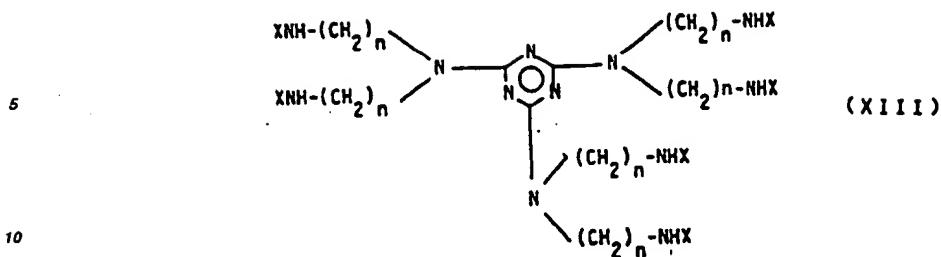


in which R₁ is C₁-C₈-alkyl, C₅-C₉-cycloalkyl, (C₁-C₄)-alkoxy propyl, dimethylaminopropyl or diethylaminopropyl,

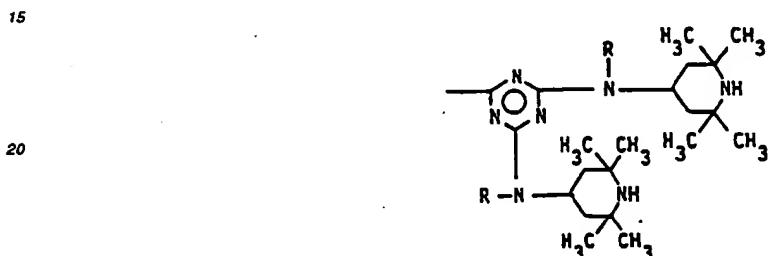
R₂ is C₂-C₆-alkylene and n is a number from 2 to 20;

(A12) The compounds claimed in European Patent 44,499, preferably those of the formula (XIII)

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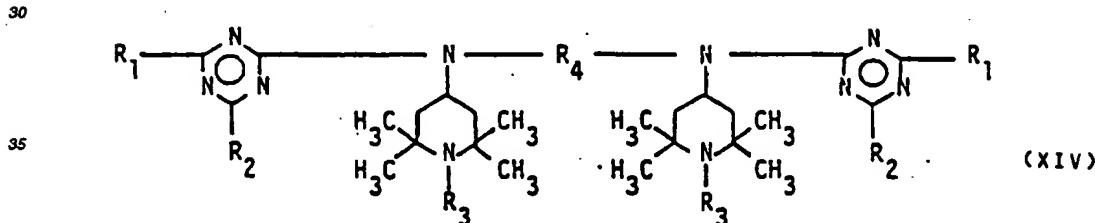


in which n is 2 or 3 and X is a group of the formula

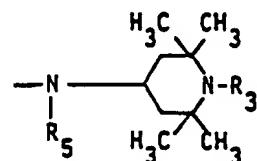


where R is hydrogen, C₁-C₈-alkyl, C₂-C₄-alkyl substituted by C₁-C₄-alkoxy or by di(C₁-C₄-alkyl)amino, or is cyclohexyl;

(A13) The compounds claimed in European Patent 70,386, preferably those of the formula (XIV)

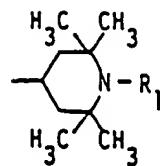


in which R₁ is allyloxy, allylamino or diallylamino, R₂ is C₁-C₄-alkoxy, allyloxy, allylamino, diallylamino, C₁-C₈-alkylamino, C₂-C₈-dialkylamino, morpholino or a group

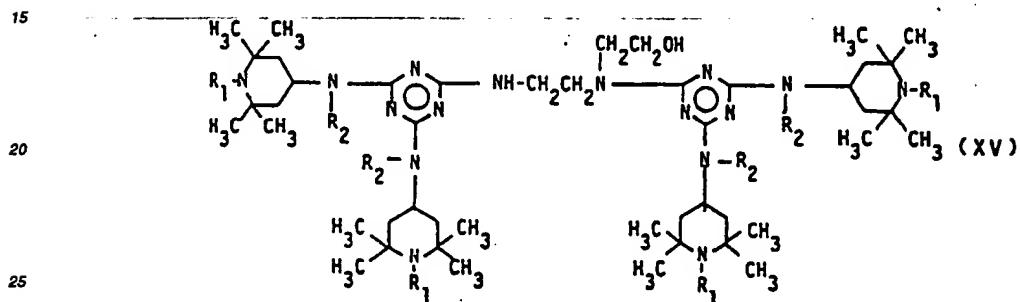


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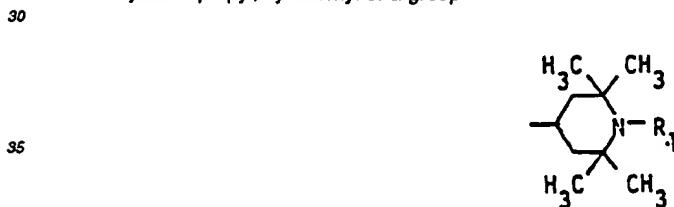
R₃ is hydrogen or methyl, R₅ is hydrogen, C₁-C₈-alkyl or a group



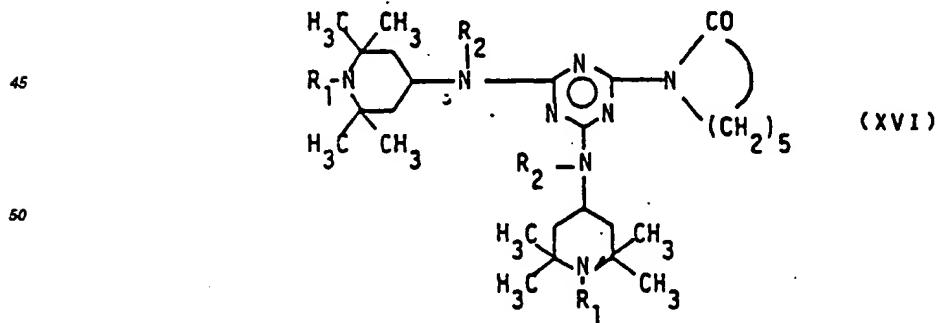
10 and R₄ is C₂-C₆-alkylene;
 (A14) The polymers claimed in US Patents 4,413,093 and 4,435,555, obtained from compounds of the formula (XIV);
 (A15) The compounds claimed in European Patent 72,009, preferably those of the formula (XV)

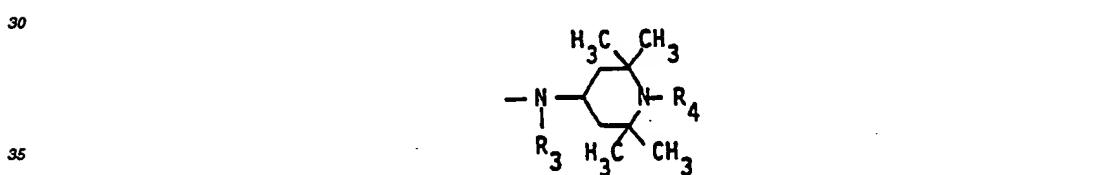
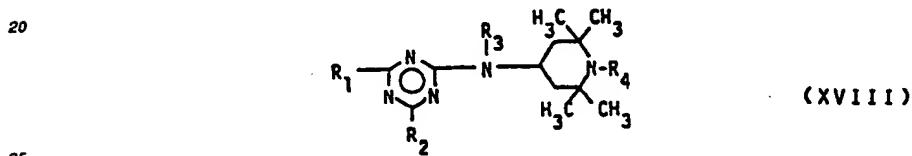
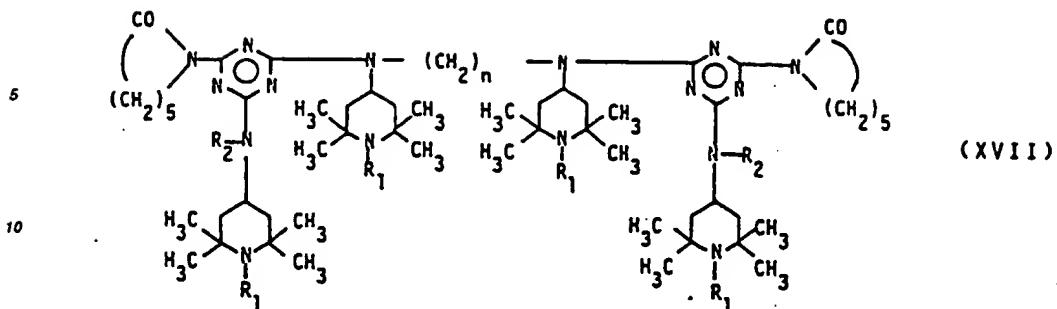


in which R₁ is hydrogen or methyl, R₂ is hydrogen, C₁-C₈-alkyl, (C₁-C₄)-alkoxypropyl, dimethylaminopropyl, diethylaminopropyl, cyclohexyl or a group

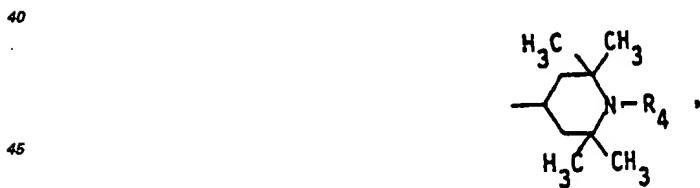


40 (A16) The compounds claimed in European Patent 75,849, preferably those of the formulae (XVI) and (XVII)





R₃ is hydrogen, C₁-C₈-alkyl or a group

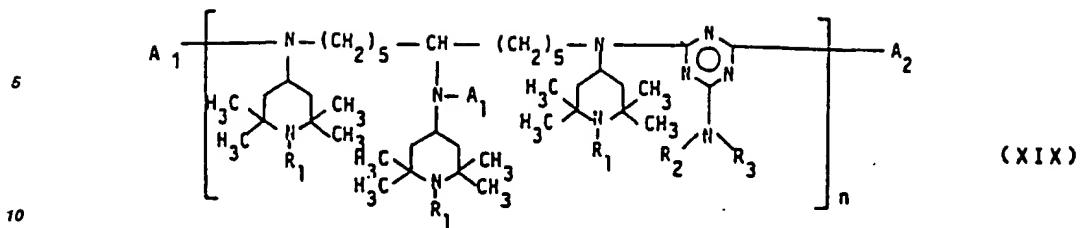


and R₄ is hydrogen or methyl;

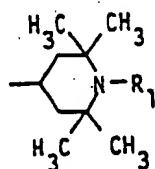
(A18) The compounds claimed in European Patent 94,048, preferably those of the formulae (XIX) and (XX)

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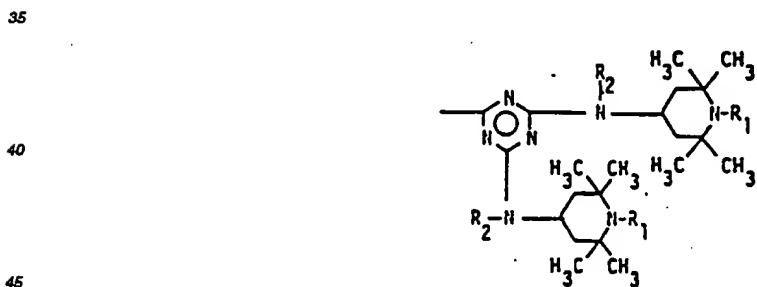
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in which n is a number from 1 to 10, R_1 is hydrogen or methyl, R_2 and R_3 which can be identical or different are $\text{C}_1\text{-C}_8\text{-alkyl}$ or a group



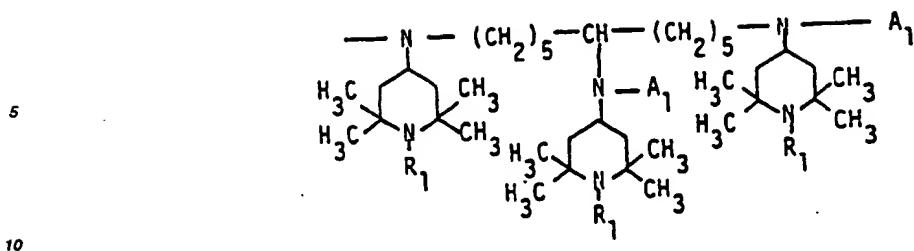
A_1 and A'_1 are hydrogen or a group



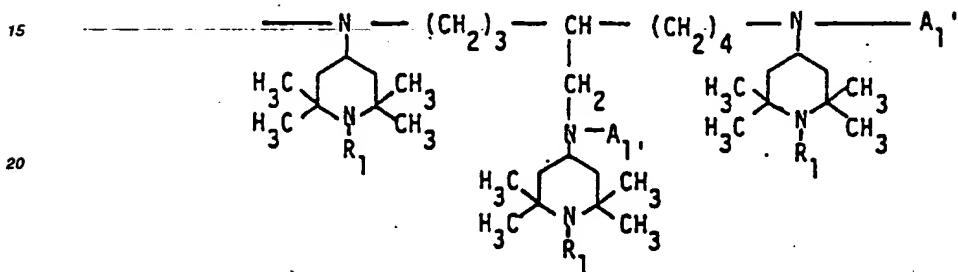
and A_2 and A'_2 are a group



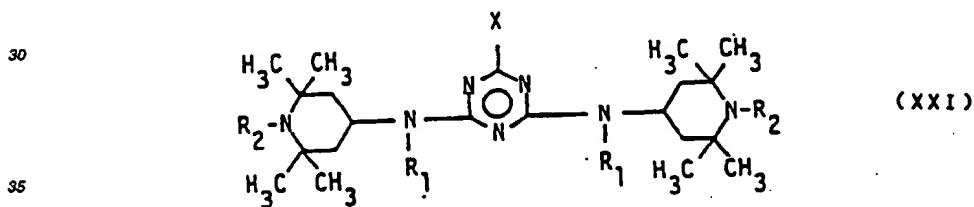
or A_2 is a group



and A'_2 is a group



(A19) The compounds claimed in European Patent 107,615, preferably those of the formula (XXI)



in which R_1 is C_1 - C_8 -alkyl, cyclohexyl, benzyl or C_2 - C_4 -alkyl substituted by C_1 - C_4 -alkoxy or dimethylamino or diethylamino, R_2 is hydrogen or methyl, X is morpholino or a group

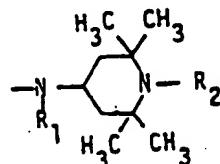
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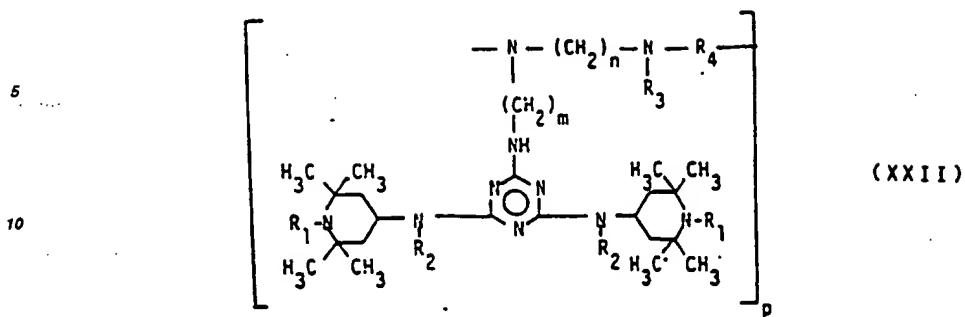
$-OR_5$ or a group

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55 where R_3 and R_4 which can be identical or different are C_1 - C_8 -alkyl, cyclohexyl, benzyl or C_2 - C_4 -alkyl substituted by OH, C_1 - C_4 -alkoxy, dimethylamino or diethylamino, R_4 can also be hydrogen and R_5 is C_1 - C_8 -alkyl, allyl, cyclohexyl or benzyl;

(A20) The compounds claimed in US Patent 4,477,615, preferably those of the formula (XXII)

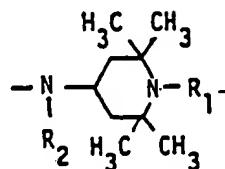


in which m and n which can be identical or different are numbers from 2 to 6; p is a number from 2 to 20, R₁ is hydrogen or methyl, R₂ is hydrogen, C₁-C₈-alkyl, cyclohexyl or benzyl, R₃ is hydrogen or a group of the formula

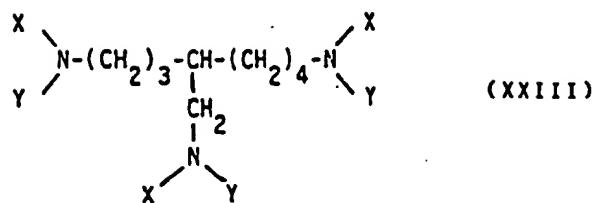
R₄ is C₂-C₆-alkylene, xylylene, 2-hydroxytrimethylene or a group of the formula



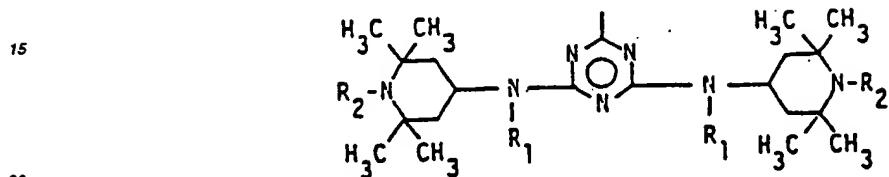
where R₅ is C₁-C₈-alkoxy, phenoxy, C₁-C₈-alkylamino, di(C₁-C₄-alkyl)amino, cyclohexylamino, morpholino or a group



(A21) The compounds claimed in US Patent 4,533,688, preferably those of the formula (XXIII)



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in which X is a group of the formula



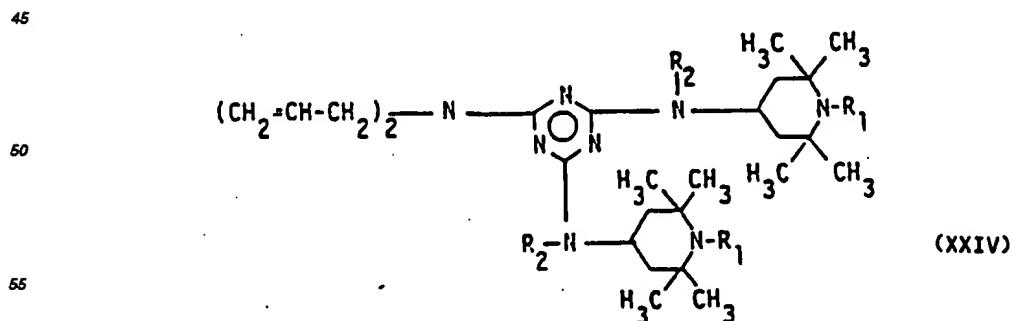
where R1 is hydrogen, C1-C8-alkyl, C3-C8-alkoxyalkyl, benzyl or a group



R2 is hydrogen or methyl and Y is hydrogen or a group



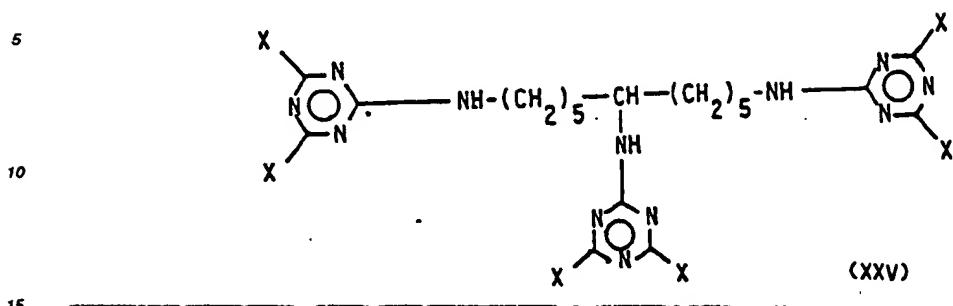
(A22) The compounds claimed in US Patent 4,540,728, preferably those of the formula (XXIV)



in which R1 is hydrogen or methyl and R2 is hydrogen or C1-C8 alkyl, and also the corresponding polymers of a

molecular weight between 800 and 5,000;

(A23) The compounds claimed in European Patent 176,106, preferably those of the formula (XXV)



in which X is a group

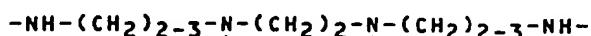
where R₁ is hydrogen or methyl and R₂ is hydrogen or C₁-C₈-alkyl.

Preferred compounds (A) are those of the formulae (II), (III), (IV), (V), (X) and (XXI).

30 Particularly preferred compounds (A) are those of the formula (II) in which R₁ is C₂-C₈-alkyl or cyclohexyl, R₂ is hydrogen or C₂-C₈-alkyl, R₃ is hydrogen or methyl, R₄ is -(CH₂)₂₋₆ and n is a number from 2 to 10, those of the formula (III) in which R₁ is hydrogen or methyl, R₂ is -(CH₂)₆, R₃ is -(CH₂)₂₋₆ and n is a number from 2 to 10, those of the formula (IV) in which R₁ is hydrogen or methyl, R₂ is C₁-C₄-alkyl, n is 2, 3 or 4 and R₃ is a group of the formula -NH-(CH₂)₂₋₆NH- for n = 2,



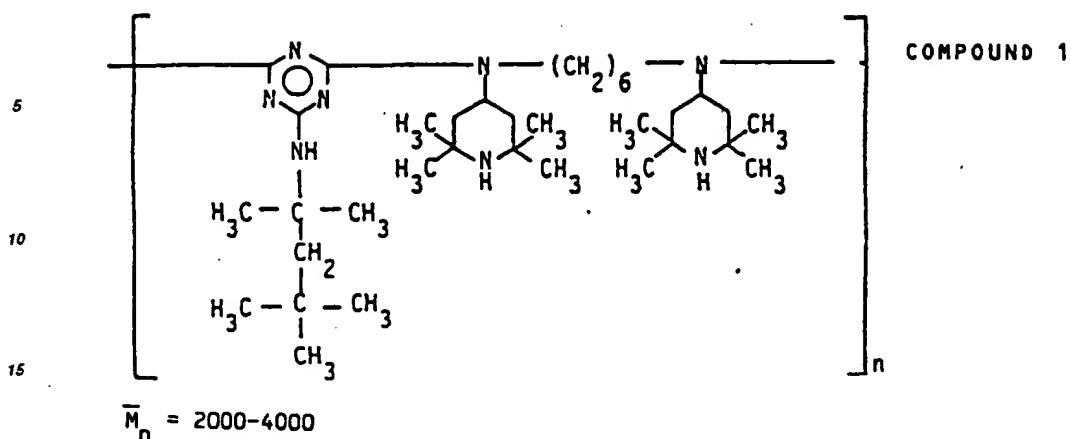
NH- for n = 3 and

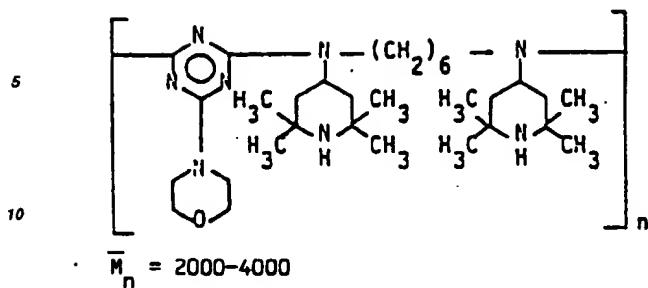


45 for n = 4, those of the formula (V) in which R is -(CH₂)₂₋₆- and n is a number from 2 to 20, those of the formula (X) in which R₁ is hydrogen or methyl, R₂ is -(CH₂)₂₋₆- and n is a number from 2 to 10, and those of the formula (XXI) in which R₁ is C₁-C₈-alkyl, R₂ is hydrogen or methyl and X is a group

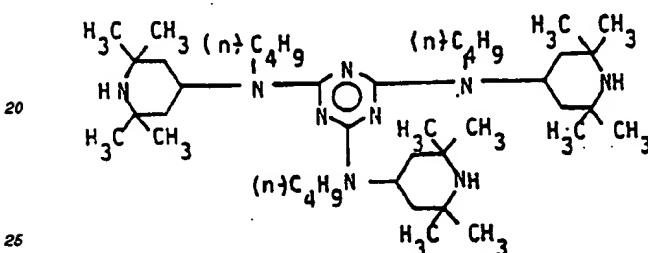


Compounds (A) of particular interest are:





COMPOUND 5



COMPOUND 6

The said compounds can be used by themselves or as a mixture with one another.

Compounds (B) which can be used according to the present invention are preferably the oxides and hydroxides of Mg and Zn.

The oxides of Mg and Zn are particularly preferred, and they can be used by themselves or as a mixture with one another.

The compounds (C) which can be used according to the present invention, if desired, are preferably salts of Al, Ca, Mg and Zn with C₁₂-C₁₈-carboxylic acids.

The stearates of Ca, Mg and Zn, which can be used by themselves or as a mixture with one another, are particularly preferred.

The percentages by weight, relative to the weight of the polyethylene, of compounds (A), (B) and (C) are: 0.025 to 2%, preferably 0.05 to 1%, for compounds (A), 0.005 to 1%, preferably 0.025 to 0.5%, for compounds (B) and 0.005 to 1%, preferably 0.025 to 0.5%, for compounds (C).

The compounds (A), (B) and (C) can be mixed with one another before they are added to the polymer, or they can be added separately to the polymer, using any one of the known processes.

If desired, other additives conventional for polyethylene, such as phenolic antioxidants, phosphites, UV absorbers and other types of light stabilizers, can be added to the compounds (A), (B) and (C) of the present invention.

Examples of additives which can be mixed with the compounds (A) (B) and (C) are:

45 Phenolic antioxidants from the following classes:

Alkylated monophenols, for example 2,6-di-t-butyl-4-methyl-phenol, 2-t-butyl-4,6-dimethylphenol, 2,6-di-t-butyl-4-ethyl-phenol, 2,6-di-t-butyl-4-n-butylphenol, 2,6-di-t-butyl-4-isobutylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-(α -methyl-cyclohexyl)-4,6-dimethylphenol, 2,6-di-octadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-t-butyl-4-methoxymethylphenol and 2,6-dinonyl-4-methylphenol.

Alkylated hydroquinones, for example 2,6-di-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,5-di-t-amylohydroquinone and 2,6-diphenyl-4-octadecyloxyphenol.

Thiobisphenols, for example 2,2'-thio-bis-(6-t-butyl-4-methylphenol), 2,2'-thio-bis-(4-octylphenol), 4,4'-thio-bis-(6-t-butyl-3-methylphenol) and 4,4'-thio-bis-(6-t-butyl-2-methylphenol).

Alkylidene-bisphenols, for example 2,2'-methylene-bis-(6-t-butyl-4-methylphenol), 2,2'-methylene-bis-(6-t-butyl-4-ethylphenol), 2,2'-methylene-bis-[4-methyl-6-(α -methylcyclohexyl)-phenol], 2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol), 2,2'-methylene-bis-(6-nonyl-4-methylphenol), 2,2'-methylene-bis-(4,6-di-t-butylphenol), 2,2'-ethyli-

5 dene-bis-(4,6-di-t-butylphenol), 2,2'-ethylidene-bis-(6-t-butyl-4-isobutylphenol), 2,2'-methylene-bis-[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis-(6-(α , α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylene-bis-(2,6-di-t-butylphenol), 4,4'-methylene-bis-(6-t-butyl-2-methylphenol), 1,1-bis-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, 2,6-bis-(3-t-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, 1,1-bis-(5-t-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis-C3,3-bis-(3'-t-butyl-4'-hydroxy-phenyl)-butyrate), bis-(3-t-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene and bis-[2-(3'-t-butyl-2'-hydroxy-5'-methylbenzyl)-6-t-butyl-4-methylphenyl] terephthalate.

10 Benzyl compounds, for example 1,3,5-tris-(3,5-di-t-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis-(3,5-di-t-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-t-butyl-4-hydroxybenzyl-mercaptoacetate, bis-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) dithiobis(terephthalate), 1,3,5-tris-(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, dioctadecyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate, calcium monoethyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate and 1,3,5-tris-(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate.

15 Acylaminophenols, for example lauric acid 4-hydroxyanilide, stearic acid 4-hydroxyanilide, 2,4-bis-(octylmercapto)-6-(3,5-di-t-butyl-4-hydroxyanilino)-s-triazine and octyl N-(3,5-di-t-butyl-4-hydroxyphenyl)-carbamate.

20 Esters of β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris-(hydroxyethyl) isocyanurate, thioglycol and N,N'-bis-(hydroxyethyl)-oxamide.

25 Esters of β -(3,5-di-cyclohexyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris-(hydroxyethyl) isocyanurate, thioglycol and N,N'-bis-(hydroxyethyl)-oxamide.

30 Amides of β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid, for example N,N'-bis-(3,5-di-t-butyl-4-hydroxyphenyl-propionyl)-hexamethylenediamine, N,N'-bis-(3,5-di-t-butyl-4-hydroxy-phenylpropionyl)-trimethylenediamine and N,N'-bis-(3,5-di-t-butyl-4-hydroxyphenylpropionyl)-hydrazine.

UV absorbers and light stabilizers

35 2-(2'-Hydroxyphenyl)-benzotriazoles, for example the 5'-methyl, 3',5'-di-t-butyl, 5'-butyl, 5'-(1,1,3,3-tetramethylbutyl), 5-chloro-3',5'-di-t-butyl, 5-chloro-3'-t-butyl-5'-methyl, 3'-sec.-butyl-5'-t-butyl, 4'-octoxy-3',5'-di-t-amyl and 3',5'-bis-(α , α -dimethylbenzyl) derivatives.

40 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

45 Esters of various substituted benzoic acids, for example 4-t-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis-(4-t-butylbenzoyl)-resorcinol, benzoylresorcinol, 2,4-di-t-butylphenyl 3,5-di-t-butyl-4-hydroxybenzoate and hexadecyl 3,5-di-t-butyl-4-hydroxybenzoate.

50 Acrylates, for example ethyl α -cyano- β , β -diphenyl-acrylate, isooctyl α -cyano- β , β -diphenylacrylate, methyl α -carboxymethoxy-cinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carboxymethoxy-p-methoxycinnamate and N-(β -carboxymethoxy- β -cyanovinyl)-2-methyl-indoline.

55 Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3bis-[4-(1,1,3,3-tetramethylbutyl)-phenol)], such as the 1:1 or 1:2 complexes, which may contain additional ligands such as n-butylamine, triethanolamine or N-cyclohexylidethanolamine, nickel dibutylidithiocarbamate, nickel salts of monoalkyl esters of 4-hydroxy-3,5-di-t-butylbenzylphosphonic acid, such as the methyl or ethyl esters, nickel complexes of ketoximes such as 2-hydroxy-4-methylphenyl undecyl ketoxime and nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

60 oxalic acid diamides, for example 4,4'-diocetyl oxanilide, 2,2'-diocetyl-5,5'-di-t-butyl oxanilide, 2,2'-diododecyl-oxo-5,5'-di-t-butyl oxanilide, 2-ethoxy-2'-ethoxyanilide, N,N'-bis-(3-dimethylaminopropyl)-oxamide, 2-ethoxy-5-t-butyl-2'-ethoxyanilide and its mixtures with 2-ethoxy-2'-ethyl-5,5'-di-t-butyl oxanilide, and mixtures of ortho- and paramethoxy and also α - and p-ethoxy-disubstituted oxanilides.

65 Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris-(nonylphenyl) phosphite, triauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris-(2,4-di-t-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis-(2,4-di-t-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis-(2,4-di-t-butylphenyl) 4,4'-diphenylenediphosphonite and 3,9-bis-(2,4-di-t-butylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane.

70 The use of the stabilizer mixtures according to the present invention is illustrated by the examples which follow; these are given by way of illustration only and do not imply any restriction.

EXAMPLES 1 - 10

10 kg of low-density polyethylene powder of melt index 0.6 (Fertene EF 3-2000, a product from Soc. Enichem Polimeri) are mixed in a slow mixer with the compounds indicated in Table 1.

5 The mixtures are then extruded at a temperature of 190°C and converted into granules, from which stretched films of 150 µm thickness are obtained by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26 D and head diameter = 100 mm) under the following working conditions:

10 body temperature = 170-190-200°C

15 head temperature = 200-200-200-190°C

The films obtained are exposed outdoors at 45°, facing south, on pinewood at Pontecchio Marconi (Bologna) (about 110 kly/year). The residual elongation is measured on samples, taken after various times of exposure by means of a constant-speed tensometer.

15 The energy received (expressed in kilolangleys) needed to halve the initial elongation value is then calculated (T_{50}). The results obtained are shown in Table 1.

TABLE 1

Example No.	Compound A (g)	Compound B (g)	Compound C (g)	T_{50} elongation (kly)
1	Compound 1 (20)	-	-	117
2	-	MgO (10)	-	168
3	-	ZnO (10)	-	138
4	-	MgO (10)	Ca stearate (10)	193
5	-	ZnO (10)	-	161
6	Compound 2 (20)	-	-	128
7	-	MgO (10)	-	175
8	-	ZnO (10)	-	154
9	-	MgO (10)	Ca stearate (10)	192
10	-	ZnO (10)	-	186

Examples 11-18

50 10 kg of low-density polyethylene powder of melt index 0.1 (Fertene EF 3-2000, a product from Soc. ENICHEM POLIMERI) are mixed in a slow mixer with the compounds indicated in Table 2.

The mixtures are then extruded at a temperature of 190°C and converted into granules, from which stretched films of 150 µm thickness are obtained by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26D and head diameter = 100 mm) under the following working conditions:

55 body temperature = 170 - 190 - 200°C

head temperature = 200 - 200 - 200 - 190°C

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The films obtained are exposed in a model 65 WR Weather - O-meter (ASTM G 26 - 77) with a black panel temperature of 63°C. The residual elongation is measured on samples, taken after various times of exposure to light, by means of a constant speed tensometer; the exposure time in hours (T_{50}) needed to halve the initial elongation value is then calculated. The results obtained are shown in Table 2:

5

Table 2

Example N°	Compound A (g)	Compound B (g)	Compound C (g)	T_{50} (hours)
10	11 compound 1 (10)	-	-	3900
	12	ZnO (5)	Ca stearate (5)	> 4500
15	13 compound 3 (10)	-	-	3600
	14	ZnO (5)	Ca stearate (5)	> 4500
20	15 compound 5 (10)	-	-	3140
	16	ZnO (5)	Ca stearate (5)	4100
25	17 compound 6 (10)	-	-	3040
	18	ZnO (5)	Ca stearate (5)	> 4500

30 Examples 19-21

10 kg of linear low-density polyethylene (LLDPE) powder of melt index 0.9 (Dowlex 2045, a product from Dow Chemical) are mixed in a slow mixer with 2 g of pentaerythritol-tetrakis [3-(3,5-di-t-butyl-4-hydroxy-phenyl)propionate], 8 g of tris-(2,4-di-t-butyl-phenyl)phosphite and with the compounds indicated in Table 3.

35

The mixtures are then extruded to give stretched films of 150 μm thickness by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26D and head diameter = 100 mm) under the following working conditions:

body temperature: 180 - 220 - 220°C

40

head temperature: 220 - 220 - 220 - 220°C

The films obtained are exposed outdoors at 45°, facing south, on pinewood at Pontecchio Marconi (Bologna) (about 110 kly/year). The residual elongation is measured on samples, taken after various times of exposure by means of a constant speed tensometer.

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The energy received (express in Kilolangleys) needed to halve the initial elongation value is then calculated (T_{50}). The results obtained are shown in Table 3.

50

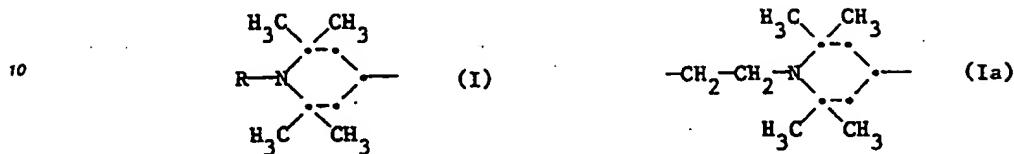
Table 3

Example No.	Compound A (g)	Compound B (g)	Compound C (g)	T_{50} elongation (Klys)
55	19 compound 1 (30)	-	-	98
	20	MgO (10)	-	135
	21	ZnO (10)	-	127

Claims

1. A light stabilizer composition for polyethylene, comprising:

5 (A) one or more compounds with piperidine groups of the formula (I) or (Ia)

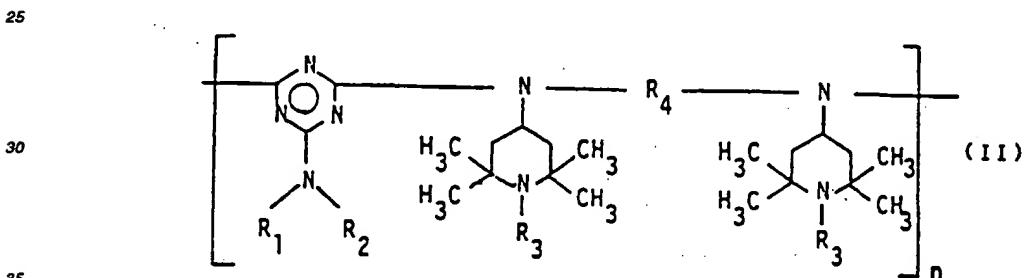


15 in which R is hydrogen, C₁-C₄-alkyl, allyl, benzyl, acetyl, acryloyl, 2-hydroxyethyl or 2-hydroxypropyl, said piperidine group of formula (I) not being bound in the 4-position to an oxygen atom, and

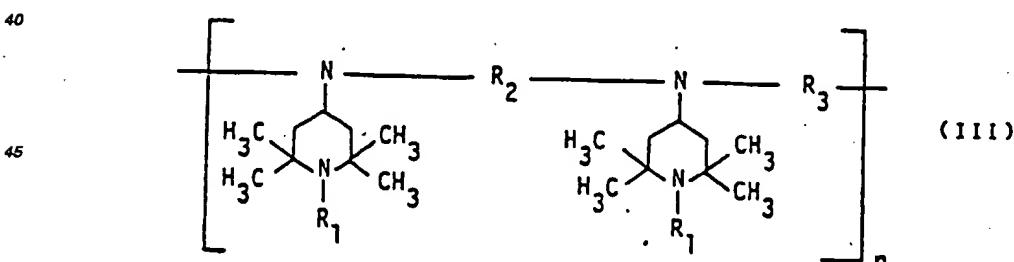
(B) one or more metal compounds selected from an oxide or hydroxide of Al, Mg and Zn.

20 2. A light stabilizer composition for polyethylene, comprising, in addition to compounds (A) and (B) of claim 1:
(C) one or more salts of Al, Ba, Ca, Mg, Sr and Zn with a C₁-C₂₂-carboxylic acid.

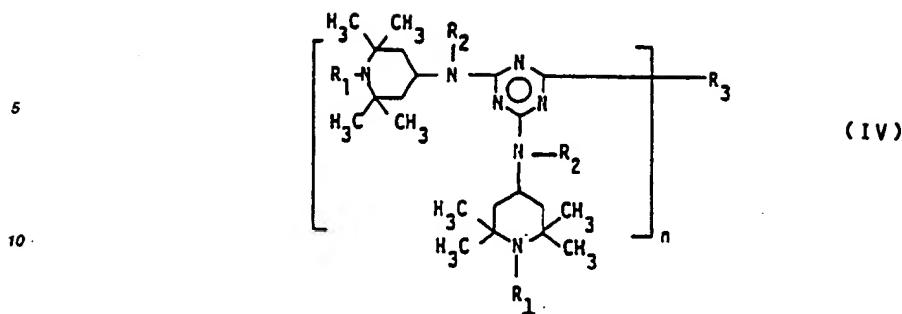
25 3. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formulae



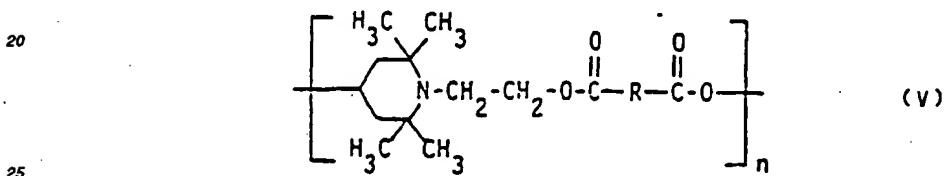
in which R₁ is C₁-C₈-alkyl, cyclohexyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, R₂ is hydrogen or C₁-C₈-alkyl, R₃ is hydrogen or methyl, R₄ is C₂-C₆-alkylene and n is a number from 2 to 20;



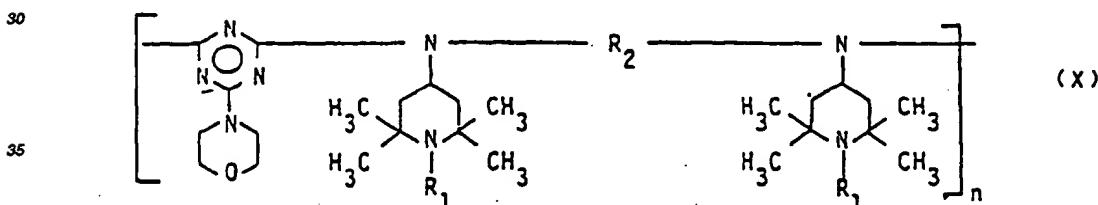
50 in which R₁ is hydrogen or methyl, R₂ is C₂-C₆-alkylene, R₃ is C₂-C₆-alkylene, 2-hydroxytrimethylene or xylylene and n is a number from 2 to 20;



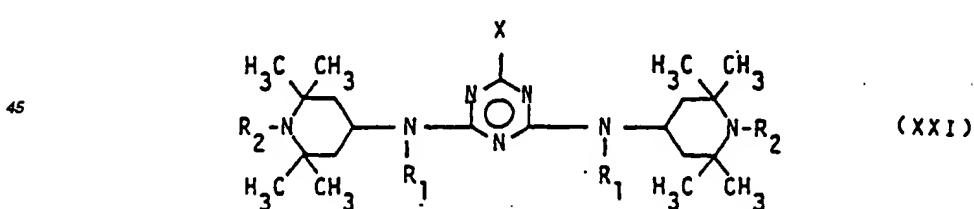
15 in which R_1 is hydrogen or methyl, R_2 is hydrogen, C_1 - C_8 -alkyl, cyclohexyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, n is 2, 3 or 4 and R_3 is the radical of an n -valent polyamine;



in which R is C_2 - C_8 -alkylene and n is a number from 2 to 30;



40 in which R_1 is hydrogen or methyl, R_2 is C_2 - C_6 -alkylene and n is a number from 2 to 20; and

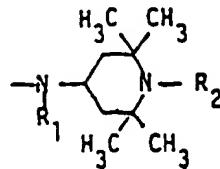


55 in which R_1 is C_1 - C_8 -alkyl, cyclohexyl, benzyl or C_2 - C_4 -alkyl substituted by C_1 - C_4 -alkoxy or dimethylamino or diethylamino, R_2 is hydrogen or methyl, X is morpholino or a group



-OR6 or a group

5



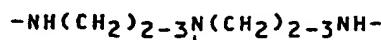
10 where R₃ and R₄ which can be identical or different are C₁-C₆-alkyl, cyclohexyl, benzyl or C₂-C₄-alkyl substituted by OH, C₁-C₄-alkoxy, dimethylamino or diethylamino, R₄ can also be hydrogen and R₅ is C₁-C₆-alkyl, allyl, cyclohexyl or benzyl.

15 4. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising compounds of the formula (II) in which R₁ is C₂-C₆-alkyl or cyclohexyl, R₂ is hydrogen or C₂-C₆-alkyl, R₃ is hydrogen or methyl, R₄ is (CH₂)₂₋₆ and n is a number from 2 to 10.

20 5. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (III) in which R₁ is hydrogen or methyl, R₂ is -(CH₂)₆-, R₃ is -(CH₂)₂₋₆- and n is a number from 2 to 10.

25 6. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (IV), in which R₁ is hydrogen or methyl, R₂ is C₁-C₄-alkyl, n is 2, 3 or 4, and R₃ is a group of the formula -NH(CH₂)₂₋₆NH- for n = 2,

25



30

for n = 3 and



35



for n = 4.

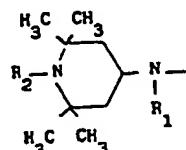
40 7. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (V), in which R is -(CH₂)₂₋₆- and n is a number from 2 to 20.

8. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (X), in which R₁ is hydrogen or methyl, R₂ is -(CH₂)₂₋₆- and n is a number from 2 to 10.

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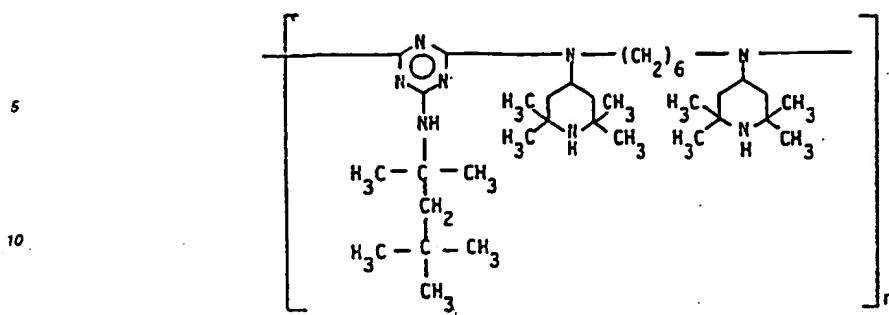
9. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (XXI), in which R₁ is C₁-C₆-alkyl, R₂ is hydrogen or methyl and X is a group

50



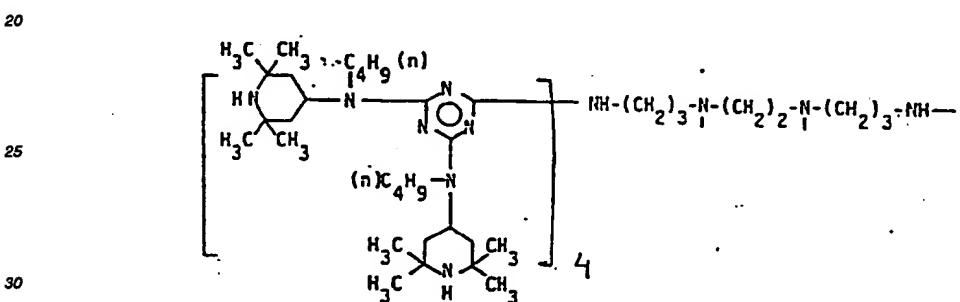
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10. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula

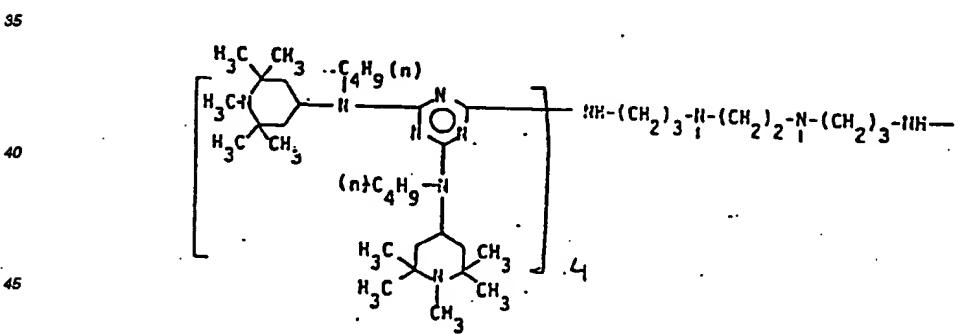


of a molecular weight between 2,000 and 4,000.

11. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula



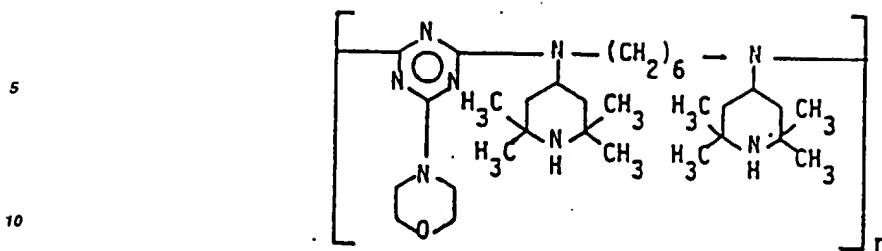
12. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula



13. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula

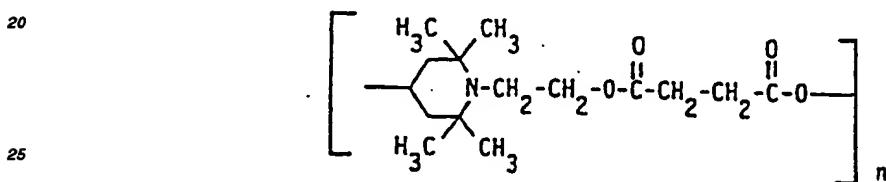
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55



of a molecular weight between 2,000 and 4,000.

15 14. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula



of a molecular weight between 2,000 and 4,000.

30 15. A light stabilizer composition according to claim 1, wherein the compound (B) is an oxide or hydroxide of Mg or Zn.

16. A light stabilizer composition according to claim 1, wherein the compound (B) is an oxide of Mg or Zn.

35 17. A light stabilizer composition according to claim 2, wherein the compound (C) is a salt of Al, Ca, Mg or Zn with C₁₂-C₁₈-carboxylic acid.

18. A light stabilizer composition according to claim 2, wherein the compound (C) is a salt of Ca, Mg or Zn with stearic acid.

40 19. Stabilized polyethylene containing a light stabilizer composition according to claim 1 or 2.

20. Stabilized polyethylene according to claim 19, wherein the percentages by weight, relative to the weight of the polyethylene, of compounds (A) and (B) are: 0.025 to 2%, preferably 0.05 to 1%, for compound (A) and 0.005 to 1%, preferably 0.025 to 0.5%, for compound (B).

45 21. Stabilized polyethylene according to claim 19, wherein the percentage by weight, relative to the polyethylene, of compound (C) is 0.005 to 1%, preferably 0.025 to 0.5%.

50 22. Stabilized polyethylene according to claim 19, which is low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) or a mixture thereof.

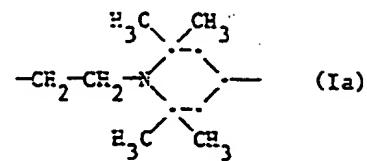
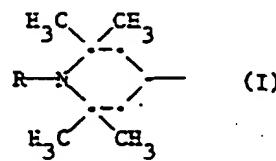
23. A film, prepared from low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) or a mixture thereof, stabilized with a light stabilizer composition of claim 1 or 2.

55

Patentansprüche

1. Lichtstabilisator-Zusammensetzung für Polyethylen, umfassend

(A) eine oder mehrere Verbindungen mit Piperidingruppen der Formel (I) oder (Ia)



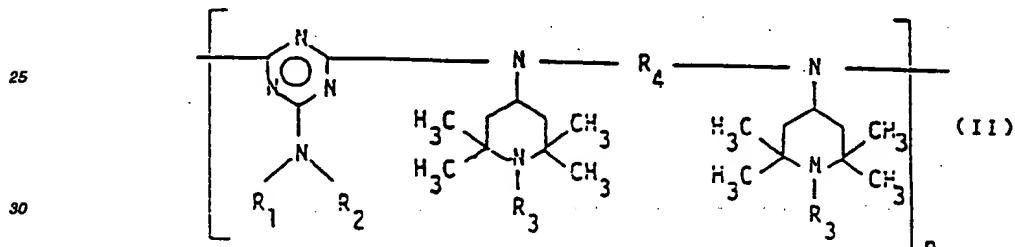
worin R Wasserstoff, C₁₋₄-Alkyl, Allyl, Benzyl, Acetyl, Acryloyl, 2-Hydroxyethyl oder 2-Hydroxypropyl bedeutet, wobei die Piperidingruppe der Formel (I) nicht in 4-Stellung an ein Sauerstoffatom gebunden ist, und

(B) eine oder mehrere Metallverbindungen, ausgewählt unter einem Oxid oder Hydroxid von Al, Mg und Zn.

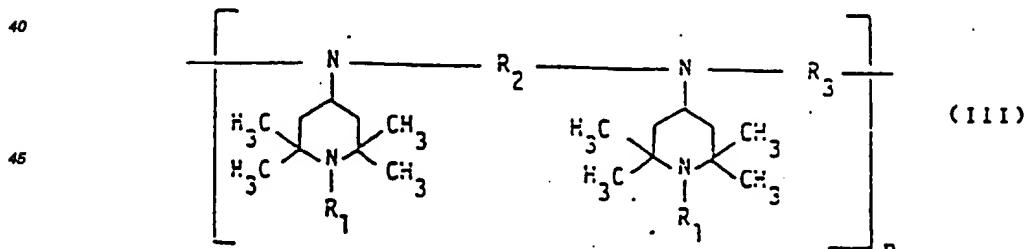
15 2. Lichtstabilisator-Zusammensetzung für Polyethylen, umfassend zusätzlich zu den Verbindungen (A) und (B) von Anspruch 1

(C) ein oder mehrere Salze von Al, Ba, Ca, Mg, Sr und Zn mit einer C₁₋₂₂-Carbonsäure.

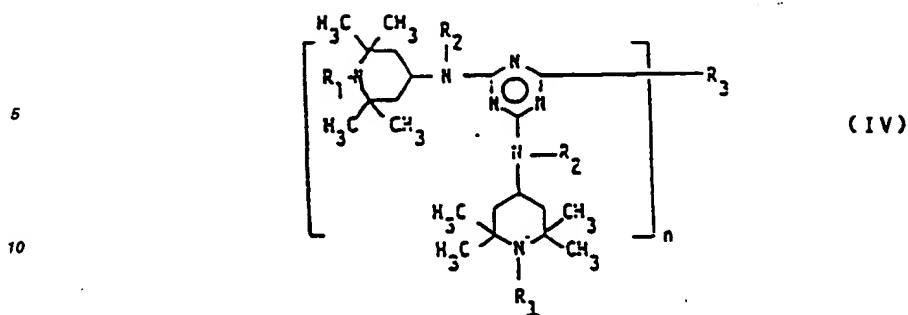
20 3. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formeln



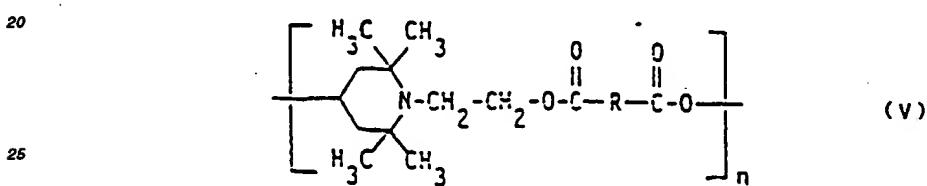
35 worin R₁ C₁₋₈-Alkyl, Cyclohexyl, 2,2,6,6-Tetramethyl-4-piperidyl oder 1,2,2,6,6-Pentamethyl-4-piperidyl bedeutet, R₂ Wasserstoff oder C₁₋₈-Alkyl ist, R₃ für Wasserstoff oder Methyl steht, R₄ für C₂₋₆-Alkylen steht und n eine Zahl von 2 bis 20 ist;



45 50 worin R₁ Wasserstoff oder Methyl bedeutet, R₂ C₂₋₆-Alkylen ist, R₃ für C₂₋₆-Alkylen, 2-Hydroxytrimethylen oder Xylylen steht und n eine Zahl von 2 bis 20 ist;

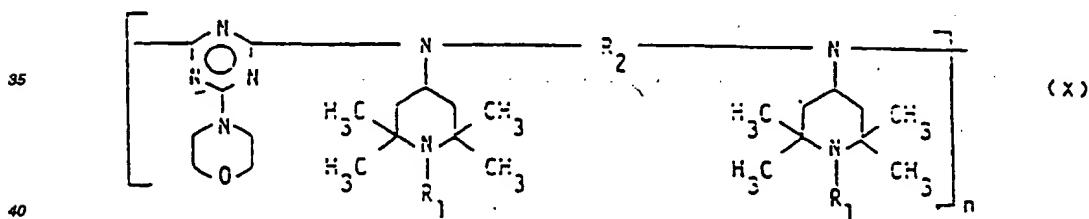


worin R_1 Wasserstoff oder Methyl bedeutet, R_2 Wasserstoff, C_{1-8} -Alkyl, Cyclohexyl, 2,2,6,6-Tetramethyl-4-piperidyl oder 1,2,2,6,6-Pentamethyl-4-piperidyl ist, n für 2, 3 oder 4 steht und R_3 den Rest eines n -wertigen Polyamins wiedergibt;

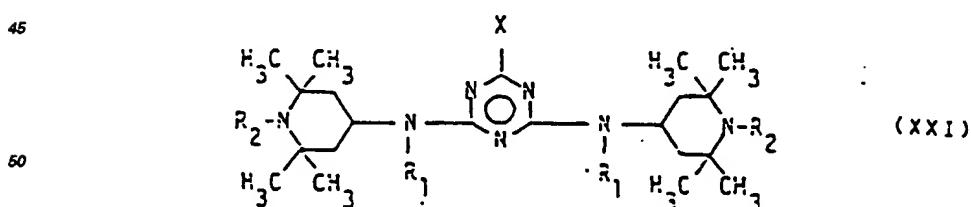


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worin R C_{2-6} -Alkylen ist und n für eine Zahl von 2 bis 30 steht;



worin R_1 Wasserstoff oder Methyl bedeutet, R_2 für C_{2-6} -Alkylen steht und n eine Zahl von 2 bis 20 ist; und



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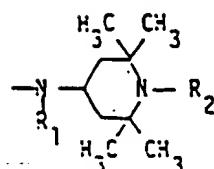
worin R_1 C_{1-8} -Alkyl, Cyclohexyl, Benzyl oder C_{2-4} -Alkyl, substituiert durch C_{1-4} -Alkoxy oder Dimethylamino oder Diethylamino, ist, R_2 für Wasserstoff oder Methyl steht, X Morpholino oder eine Gruppe



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-OR₅ oder eine Gruppe

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bedeutet, worin R₃ und R₄, die identisch oder verschieden sein können, C₁₋₈-Alkyl, Cyclohexyl, Benzyl oder C₂₋₄-Alkyl, substituiert durch OH, C₁₋₄-Alkoxy, Dimethylamino oder Diethylamino, sind, R₄ auch Wasserstoff sein kann und R₅ für C₁₋₈-Alkyl, Allyl, Cyclohexyl oder Benzyl steht.

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4. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (II), worin R₁ C₂₋₈-Alkyl oder Cyclohexyl bedeutet, R₂ Wasserstoff oder C₂₋₈-Alkyl ist, R₃ für Wasserstoff oder Methyl steht, R₄ für -(CH₂)₂₋₆- steht und n eine Zahl von 2 bis 10 ist.

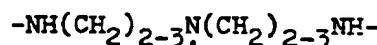
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5. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (III), worin R₁ Wasserstoff oder Methyl bedeutet, R₂ für -(CH₂)₆- steht, R₃ für -(CH₂)₂₋₆- steht und n eine Zahl von 2 bis 10 ist.

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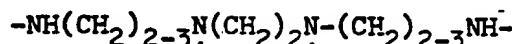
6. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (IV), worin R₁ Wasserstoff oder Methyl bedeutet, R₂ für C₁₋₄-Alkyl steht, n für 2, 3 oder 4 steht und R₃ eine Gruppe der Formel -NH(CH₂)₂₋₆NH- für n = 2,

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für n = 3 und

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für n = 4 ist.

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7. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (V), worin R für -(CH₂)₂₋₆- steht und n eine Zahl von 2 bis 20 ist.

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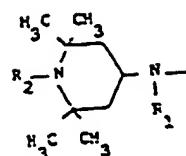
8. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (X), worin R₁ Wasserstoff oder Methyl bedeutet, R₂ für -(CH₂)₂₋₆- steht und n eine Zahl von 2 bis 10 ist.

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9. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (XXI), worin R₁ C₁₋₈-Alkyl ist, R₂ Wasserstoff oder Methyl bedeutet und X eine Gruppe

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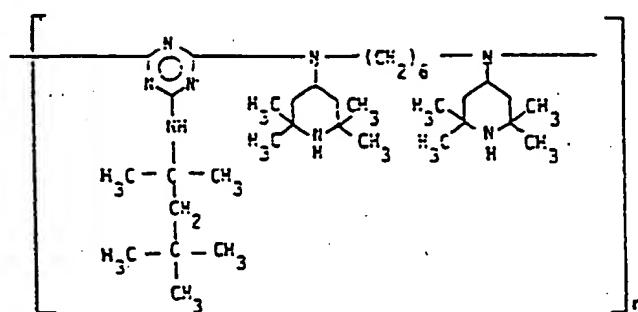
wiedergibt.

10. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) diejenige der Formel

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mit einem Molekulargewicht zwischen 2000 und 4000 ist.

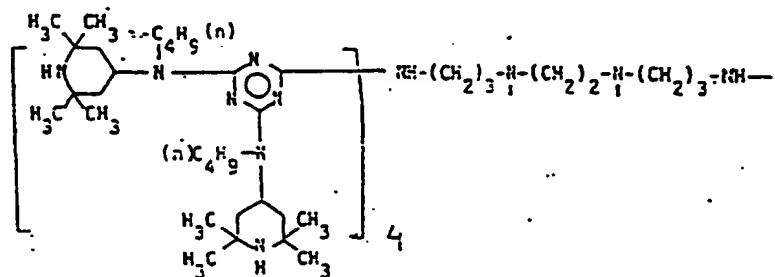
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11. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) diejenige der Formel

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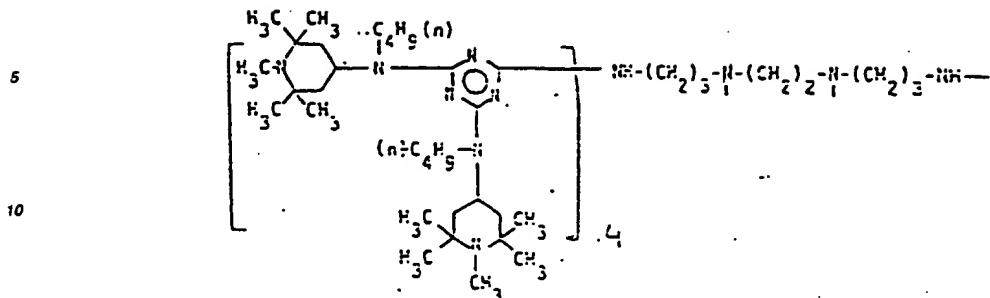


ist.

12. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) diejenige der Formel

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20. Stabilisiertes Polyethylen gemäß Anspruch 19, worin die Gewichtsprozentanteile, bezogen auf das Gewicht des Polyethylen, der Verbindungen (A) und (B) sind: 0,025 bis 2%, bevorzugt 0,05 bis 1%, für Verbindung (A) und 0,005 bis 1%, bevorzugt 0,025 bis 0,5%, für Verbindung (B).

5 21. Stabilisiertes Polyethylen gemäß Anspruch 19, worin der Gewichtsprozentanteil, bezogen auf das Polyethylen, der Verbindung (C) 0,005 bis 1%, bevorzugt 0,025 bis 0,5%, beträgt.

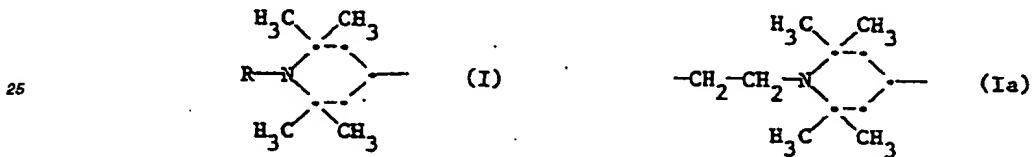
10 22. Stabilisiertes Polyethylen gemäß Anspruch 19, bei dem es sich um Polyethylen niedriger Dichte (LDPE), lineares Polyethylen niedriger Dichte (LLDPE) oder eine Mischung hiervon handelt.

23. Film, hergestellt aus Polyethylen niedriger Dichte (LDPE), linearem Polyethylen niedriger Dichte (LLDPE) oder einer Mischung hiervon, stabilisiert mit einer Lichtstabilisator-Zusammensetzung gemäß Anspruch 1 oder 2.

15 Revendications

1. Composition de photostabilisants pour le polyéthylène comprenant

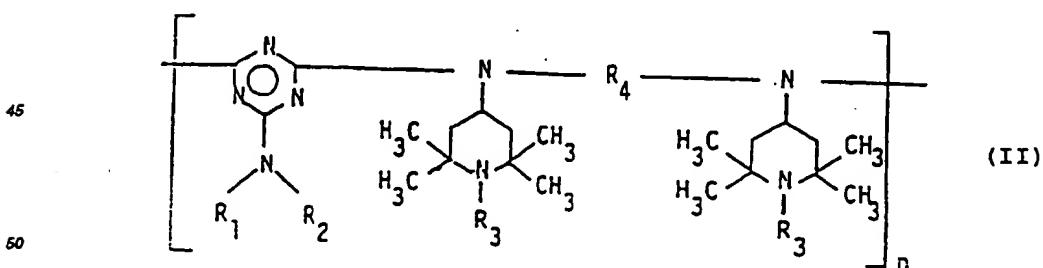
(A) un ou plusieurs composés comportant des groupes pipéridino de formule (I) ou (la)



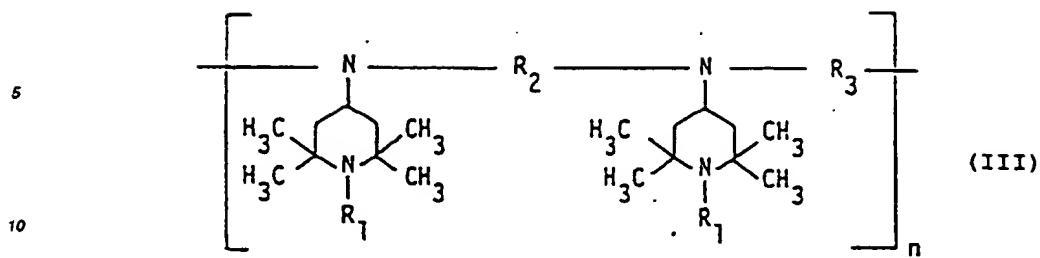
30 dans lesquelles R est l'hydrogène, alkyle en C₁-C₄, allyle, benzyle, acétyle, acryloyle, 2-hydroxyéthyle ou 2-hydroxypropyle, ledit groupe pipéridino de formule (I) n'étant pas lié en position 4 à un atome d'oxygène, et (B) un ou plusieurs composés métalliques pris parmi un oxyde ou un hydroxyde d'Al, de Mg et de Zn.

35 2. Composition de photostabilisants pour le polyéthylène comprenant en plus des composés (A) et (B) de la revendication 1 :
(C) un ou plusieurs sels d'Al, Ba, Ca, Mg, Sr et Zn avec un acide carboxylique en C₁-C₂₂.

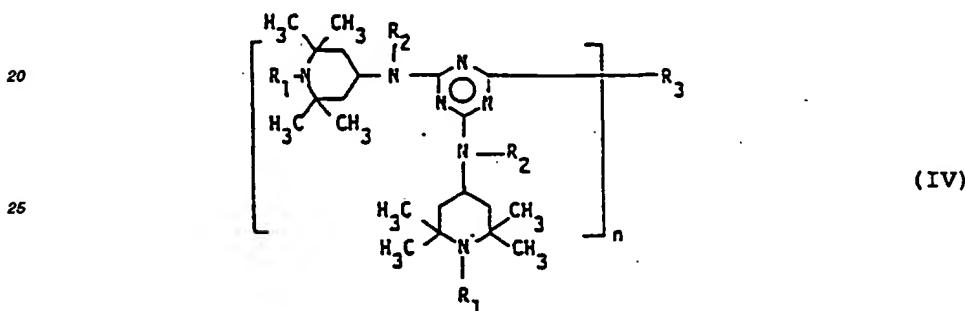
3. Composition de photostabilisants selon la revendication 1, où le composé (A) est pris dans le groupe comprenant les composés de formules



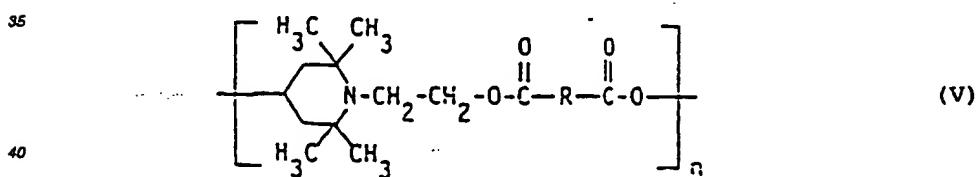
55 dans laquelle R_1 est alkyle en $C_1\text{-}C_8$, cyclohexyle, 2,2,6,6-tétraméthyl-4-pipéridyle ou 1,2,2,6,6-pentaméthyl-4-pipéridyle, R_2 est l'hydrogène ou alkyle en $C_1\text{-}C_8$, R_3 est l'hydrogène ou méthyle, R_4 est alkylène en $C_2\text{-}C_6$ et n est un nombre de 2 à 20 ;



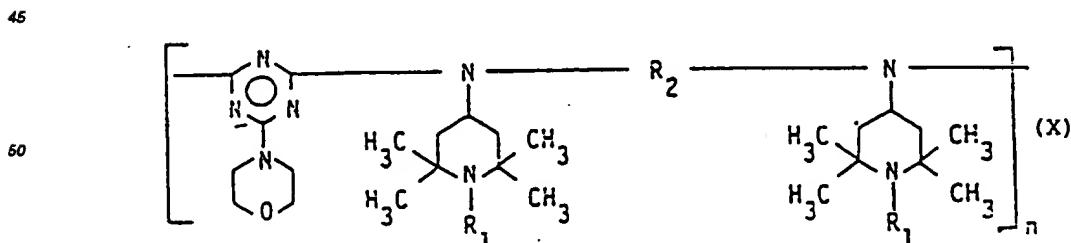
dans laquelle R₁ est l'hydrogène ou méthyle, R₂ est alkylène en C₂-C₆, R₃ est alkylène en C₂-C₆, 2-hydroxy-triméthylène ou xylylène et n est un nombre de 2 à 20 ;



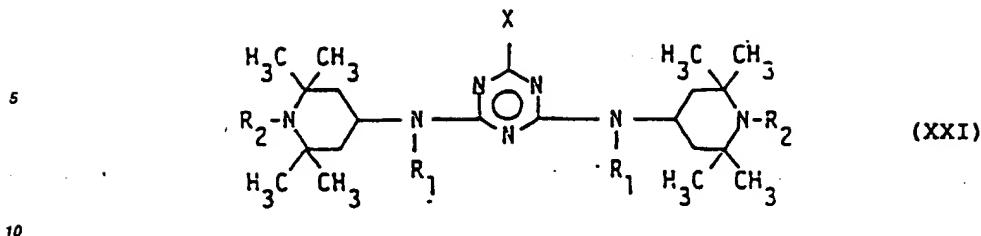
dans laquelle R₁ est l'hydrogène ou méthyle, R₂ est l'hydrogène, alkyle en C₁-C₈, cyclohexyle, 2,2,6,6-tétraméthyl-4-pipéridyle ou 1,2,2,6,6-pentaméthyl-4-pipéridyle, n vaut 2, 3 ou 4 et R₃ est le radical n-valent d'une polyamine ;



dans laquelle R est alkylène en C₂-C₈ et n est un nombre de 2 à 30 ;



dans laquelle R₁ est l'hydrogène ou méthyle, R₂ est alkylène en C₂-C₆ et n est un nombre de 2 à 20 ; et



dans laquelle R₁ est alkyle en C₁-C₈, cyclohexyle, benzyle ou alkyle en C₂-C₄ substitué par alcoxy en C₁-C₄ ou diméthylamino ou diéthylamino, R₂ est l'hydrogène ou méthyle, X est morpholino ou un groupe



20 -OR₅ ou un groupe

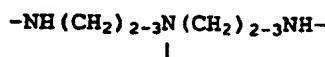


30 dans laquelle R₃ et R₄ qui peuvent être identiques ou différents sont alkyle en C₁-C₈, cyclohexyle, benzyle ou alkyle en C₂-C₄ substitués par OH, alcoxy en C₁-C₄, diméthylamino ou diéthylamino, R₄ peut être aussi l'hydrogène et R₅ est alkyle en C₁-C₈, allyle, cyclohexyle ou benzyle.

35 4. Composition de photostabilisants selon la revendication 1 où le composé (A) est pris dans le groupe comprenant des composés de formule (II) dans laquelle R₁ est alkyle en C₂-C₈ ou cyclohexyle, R₂ est l'hydrogène ou alkyle en C₂-C₈, R₃ est l'hydrogène ou méthyle, R₄ est -(CH₂)₂₋₆- et n est un nombre de 2 à 10.

40 5. Composition de photostabilisants selon la revendication 1 dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (III) dans lesquels R₁ est l'hydrogène ou méthyle, R₂ est -(CH₂)₆-, R₃ est -(CH₂)₂₋₆- et n est un nombre de 2 à 10.

45 6. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (IV) dans lesquels R₁ est l'hydrogène ou méthyle, R₂ est alkyle en C₁-C₄, n vaut 2, 3 ou 4, et R₃ est un groupe de formule -NH(CH₂)₂₋₆NH- pour n = 2,



50 pour n = 3 et



pour n = 4.

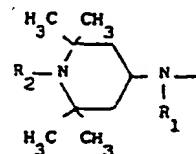
7. Composition de photostabilisants selon la revendication 1 dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (V) dans lesquels R est $-(CH_2)_{2-6}$ et n est un nombre de 2 à 20.

5 8. Composition de photophotostabilisants selon la revendication 1, dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (X) dans lesquels R₁ est l'hydrogène ou méthyle, R₂ est $-(CH_2)_{2-6}$ et n est un nombre de 2 à 10.

9. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (XXI) dans lesquels R₁ est alkyle en C₁-C₈, R₂ est l'hydrogène ou méthyle et X est un groupe

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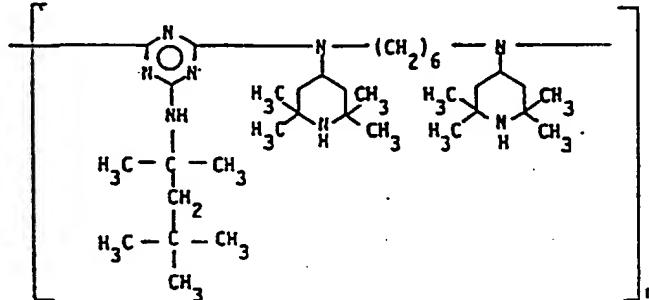


20 10. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) répond à la formule

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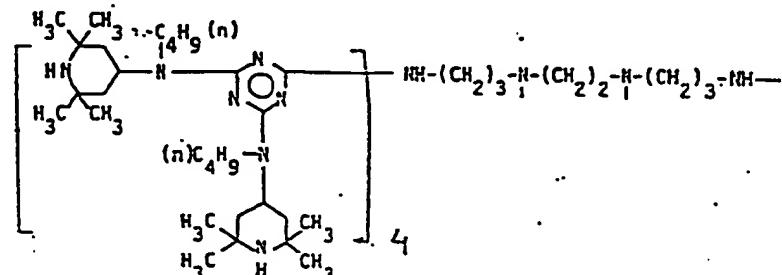


ayant une masse moléculaire comprise entre 2000 et 4000.

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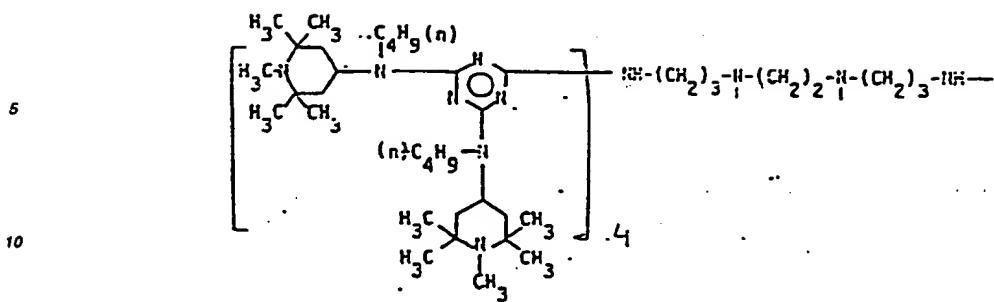
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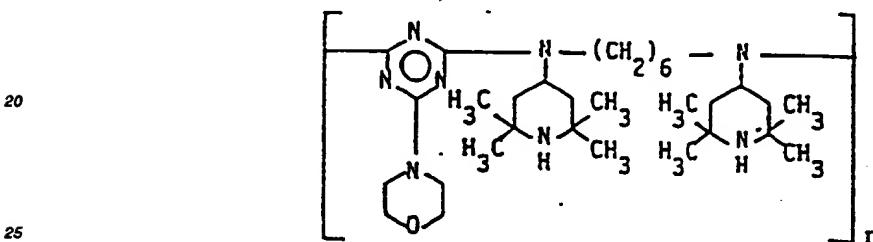
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12. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) répond à la formule



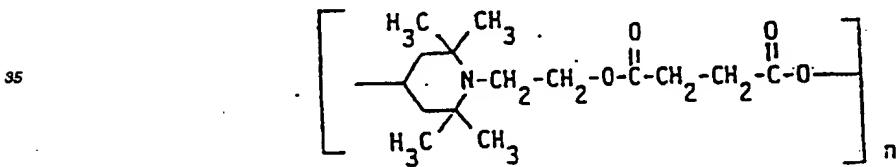
13. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) répond à la formule

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ayant une masse moléculaire comprise entre 2000 et 4000.

30 14. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) répond à la formule



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ayant une masse moléculaire comprise entre 2000 et 4000.

45 15. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (B) est un oxyde ou un hydroxyde de Mg ou de Zn.

16. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (B) est un oxyde de Mg ou de Zn.

50 17. Composition de photostabilisants selon la revendication 2, dans laquelle le composé (C) est un sel d'Al, Ca, Mg ou Zn avec un acide dicarboxylique en C12-C18.

18. Composition de photostabilisants selon la revendication 2, dans laquelle le composé (C) est un sel de Ca, Mg ou Zn avec l'acide stéarique.

55 19. Polyéthylène stabilisé contenant une composition de photostabilisants selon la revendication 1 ou 2.

20. Polyéthylène stabilisé selon la revendication 19, dans lequel les pourcentages en poids des composés (A) et (B), par rapport au poids du polyéthylène, sont : de 0,025 à 2 %, de préférence de 0,05 à 1 % pour le composé (A) et

de 0,005 à 1%, de préférence de 0,025 à 0,5 % pour le composé (B).

21. Polyéthylène stabilisé selon la revendication 19, dans lequel le pourcentage en poids du composé (C), par rapport au polyéthylène, est de 0,005 à 1 %, de préférence de 0,025 à 0,5 %.
- 5 22. Polyéthylène stabilisé selon la revendication 19 lequel est le polyéthylène basse densité (LDPE), le polyéthylène basse densité linéaire (LLDPE) ou un mélange de ces deux composés.
- 10 23. Film préparé à partir du polyéthylène basse densité (LDPE), du polyéthylène basse densité linéaire (LLDPE) ou de mélanges des deux, stabilisé par une composition de photostabilisants de la revendication 1 ou 2.

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